Supporting Information

N-heterocylic Carbene Based Mn-Electrocatalyst for Two Electron CO_2 Reduction over Proton Reduction

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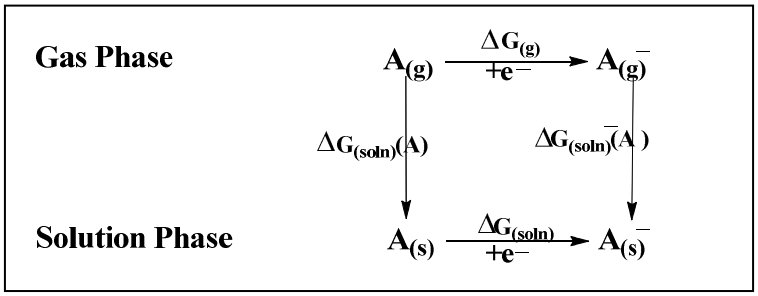
1. Gaussian full reference[45]

Gaussian 09 Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F.

Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari,A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

1. Calculation of reduction potential



3. Figure S1. Thermodynamic cycle used for reduction potential calculations.

All the reduction potentials are calculated using the well-established thermodynamic cycle (above) using the following equation:

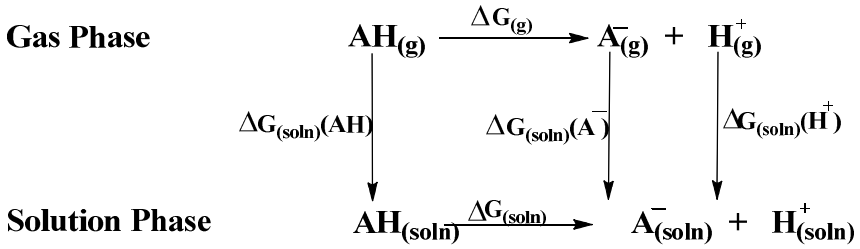
$$E = \left(-\frac{\Delta G(soln)}{nF}\right) - E^0_{ref} \qquad (1)$$

where $\Delta G(soln)$, n, F, and E^0_{ref} are the solvation (in acetonitrile solvent) free energy for the redox reaction, number of electrons, Faraday constant, and reduction potential of the reference electrode respectively. $\Delta G_{(s)}$ is modeled as following.

$$\Delta G_{(soln)} = \Delta G_{(g)} + \Delta G_{(soln)}(A^-) - \Delta G_{(soln)}(A) \qquad (2)$$

Here reference electrode is the saturated calomel electrode (SCE) and the potential is 4.67 V in acetonitrile solution.[1-2]

4. Calculation of pK_a value



5. Figure S2. Thermodynamic cycle used for the calculation of pK_a value.

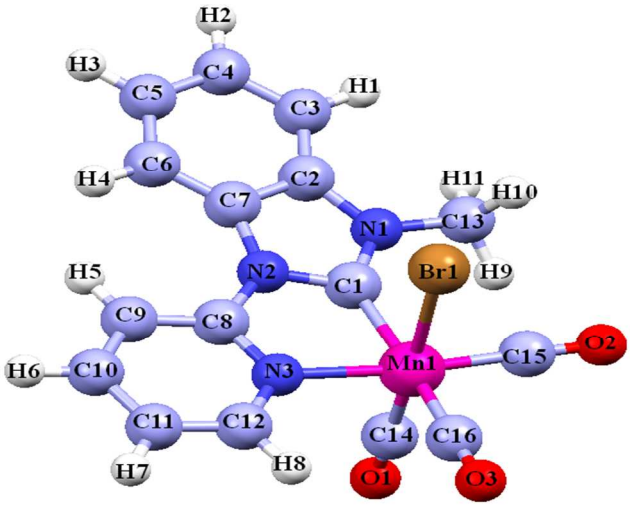
Where free energy of proton in gas phase and absolute solvation energy is taken as 6.3 kcal/mol[3] and -260.2 kcal/mol[4] respectively. The energy required to transfer a proton from gas phase to 1M solution phase in standard state is 1.89 kcal/mol.[5] Direct pK_a values are calculated using above thermodynamic cycle in acetonitrile solution, computed as:

$$\text{Direct } pK_a = \frac{\Delta G_{(s)}}{2.303RT} \qquad (4)$$

$$\Delta G(s) = G(g) + G_{(s)}(A^-) + \Delta G_{(s)}(H^+) - \Delta G_{(s)}(AH) \qquad (5)$$

Linear correction has been taken from reference 6:

$$\text{Linear correction pKa} = (\text{Direct pKa} + 7.281)/1.194 \qquad (6)$$



6. Figure S3. Optimized geometry of complex **1**.

7. Table S1. Comparisons between geometrical parameters of optimized and X-ray data of Complex 1.

Bond distances[a]	**Experimental**	**Optimized**	**Bond Angles**[b]	**Experimental**	**Optimized**
Mn1-Br1	2.5533(7)	2.577	Br1-Mn1-C14	178.19(12)	176.82
Mn1-N3	2.060(3)	2.107	Br1-Mn1-C15	88.12 (13)	87.48
Mn1-C1	1.984(4)	1.995	Br1-Mn1-C16	88.80(14)	88.07
Mn1-C14	1.794(4)	1.792	Br1-Mn1-C1	86.18(9)	81.86
Mn-C15	1.795(5)	1.806	Br1-Mn1-N3	87.26(8)	86.90
Mn-C16	1.828(5)	1.838	C1-Mn1-N3	78.41(12)	77.85
C14-O1	1.137(5)	1.160	C15-Mn1-C16	88.9(2)	89.39
C15-O2	1.158(5)	1.156	C14-Mn1-C16	92.3 (2)	95.07

[a] all bond distances are in angstrom (Å).

[b] all bond angles are in degree (°).

8-a. Reduction: In absence of CO_2 Environment

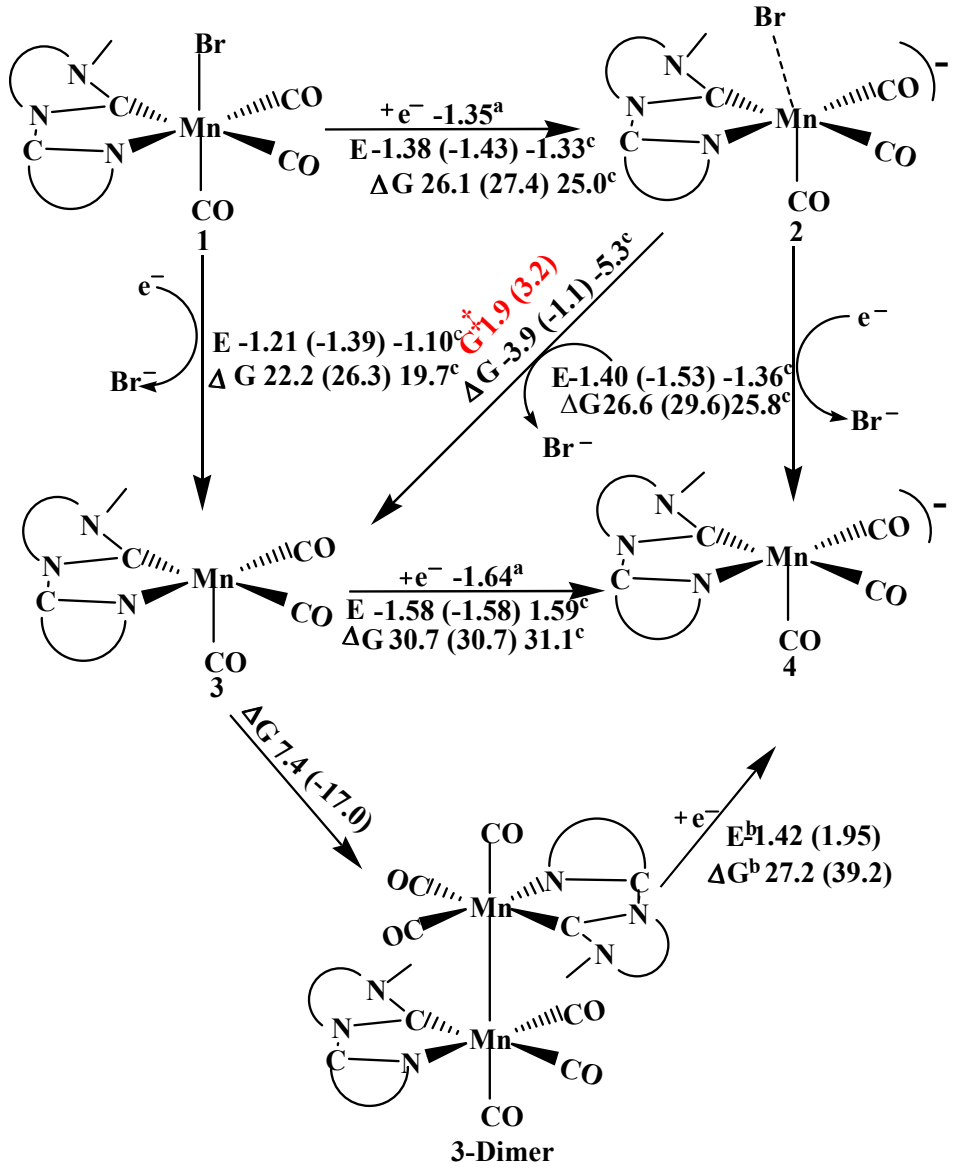


Figure S4. The calculated reaction free energies (ΔG in kcal/mol), activation barriers ($\Delta G^{\ddagger}$ in kcal/mol) and reduction potentials (E) are reported for the possible products after one- and two-electron reductions of complex **1** (in the inert environment). Values in parentheses are

calculated using GD3. [a]Experimentally reported reduction[43]. [c] Calculated using aug-cc-pVDZ basis set for all atoms except for Mn, where LANL2DZ basis set is used (Single Point) [b]Reduction potential is calculated using the equation as: $\frac{1}{2}(3\text{Dimer}) + e^- \rightarrow 4$.

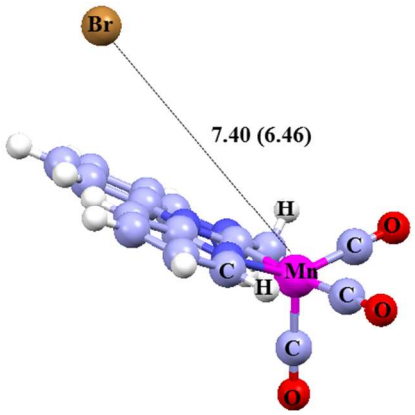


Figure S5. Transition state structure for the Bromide ion dissociation from **2**.Bond distances are in Å.Value in parentheses is calculated using GD3

8(b). Reduction: In CO_2 Environment

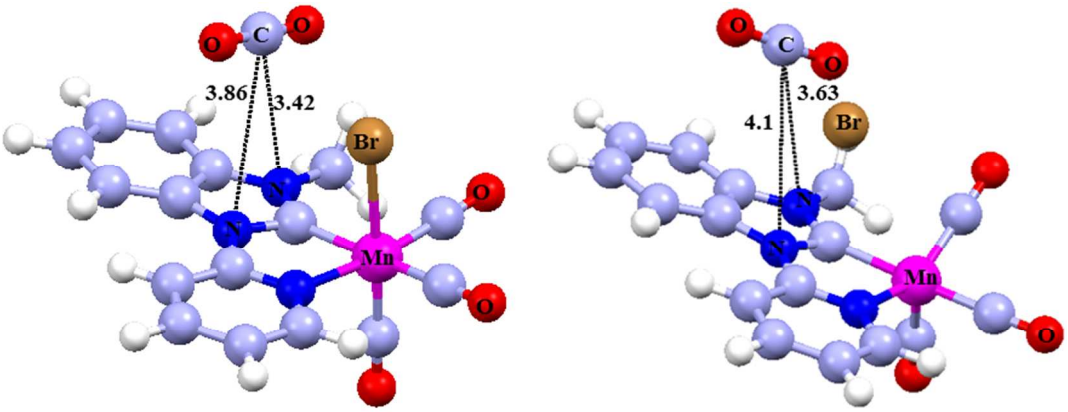


Figure S6. Interactions between the NHC-pyridine ligand and CO_2 molecule in complex **1-CO_2**

8(c.)-

Table S2. The binding (E_B) and reaction free energies (ΔG) are calculated* for CO_2 binding with **1**, **2**, **3** and **4** complexes. Values in the parentheses are calculated using Grimme's dispersion corrections (GD3).

Reaction Steps	**E_B (kcal/mol)**	ΔG **(kcal/mol)**
$1 + CO_2 \rightarrow$ 1-CO_2	-0.67 (-5.2)	4.5 (3.7)
$2 + CO_2 \rightarrow$ 2-CO_2	-0 .76 (-5.3)	6.7 (4.3)
$3 + CO_2 \rightarrow$ 3-CO_2	-0.43 (-4.9)	6.3 (3.3)
$4 + CO_2 \rightarrow$ 4-CO_2	-29.88 (-34.7)	4.9 (-0.04)

*The binding energies are calculated using the following formula:

$E_B = E_{complex\text{-}CO2} - E_{Complex} + E_{CO2}$

where $E_{complex\text{-}CO2}$ is the total energy (from optimized complex) of the CO_2 bonded complex (such as **1-CO_2, 2-CO_2, 3-CO_2** and **4-CO_2**), $E_{complex}$ is the single point energy of the complex within the geometry $E_{complex\text{-}CO2}$ and E_{CO2} is the single point energy of the CO_2 within the geometry of $E_{complex\text{-}CO2}$.

Similarly, the free energy for the CO_2 binding is calculated using the following formula:

$\Delta G = G_{complex\text{-}CO2} - G_{complex} + G_{CO2}$

where $G_{complex\text{-}CO2}$, $G_{complex}$, G_{co2} are the total free energy (with zero point and entropy corrections) of the CO_2 bonded complex (such as **1-CO_2, 2-CO_2, 3-CO_2 and 4-CO_2**), complex (such as **1**, **2**, **3** and **4**) and CO_2 respectively.

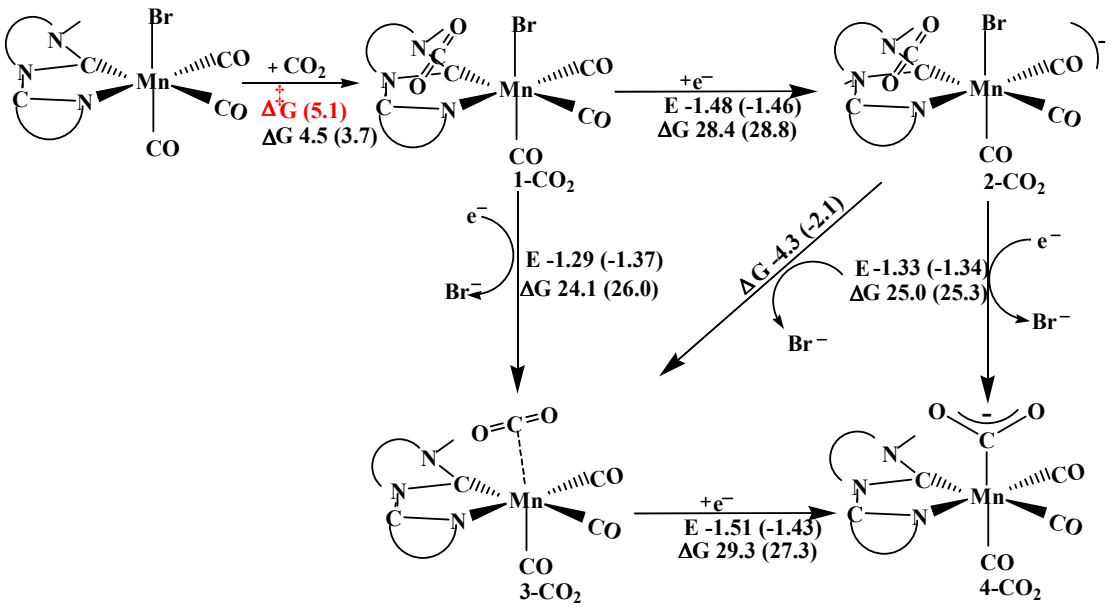


Figure S7. The calculated reaction free energies (ΔG in kcal/mol) and reduction potentials (E) are listed for possible products after one- and two-electron reductions of complex **1** (in the CO_2 environment). Values in the parentheses are calculated using GD3.

9. Reduction: In H_2O Environment

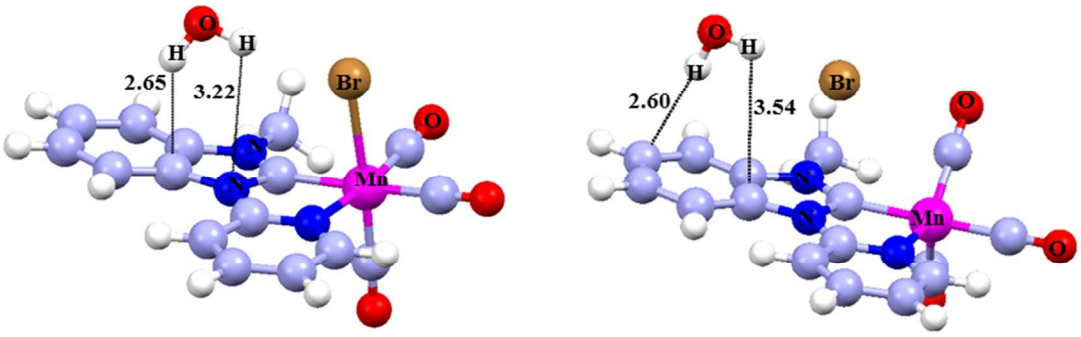


Figure S8. Interactions between the NHC-pyridine ligand and H_2O molecule in complex **1-H_2O 9(b).**

Table S3. The binding (E_B) and reaction free energies (ΔG) are tabulated for H_2O binding with **1**, **2**, **3** and **4** complexes. Values in parentheses are calculated using Grimme's dispersion corrections (GD3).

Reaction Steps	**E_B (kcal/mol)**	ΔG **(kcal/mol)**
$1 + H_2O \rightarrow$ 1-H_2O	-3.4 (-6.7)	4.5 (3.5)
$2 + H_2O \rightarrow$ 2-H_2O	-5.0 (-8.3)	4.6 (2.7)
$3 + H_2O \rightarrow$ 3-H_2O	-1.8 (-5.1)	5.7 (3.9)
$4 + H_2O \rightarrow$ 4-H_2O	-4.6 (-8.9)	4.5 (0.9)

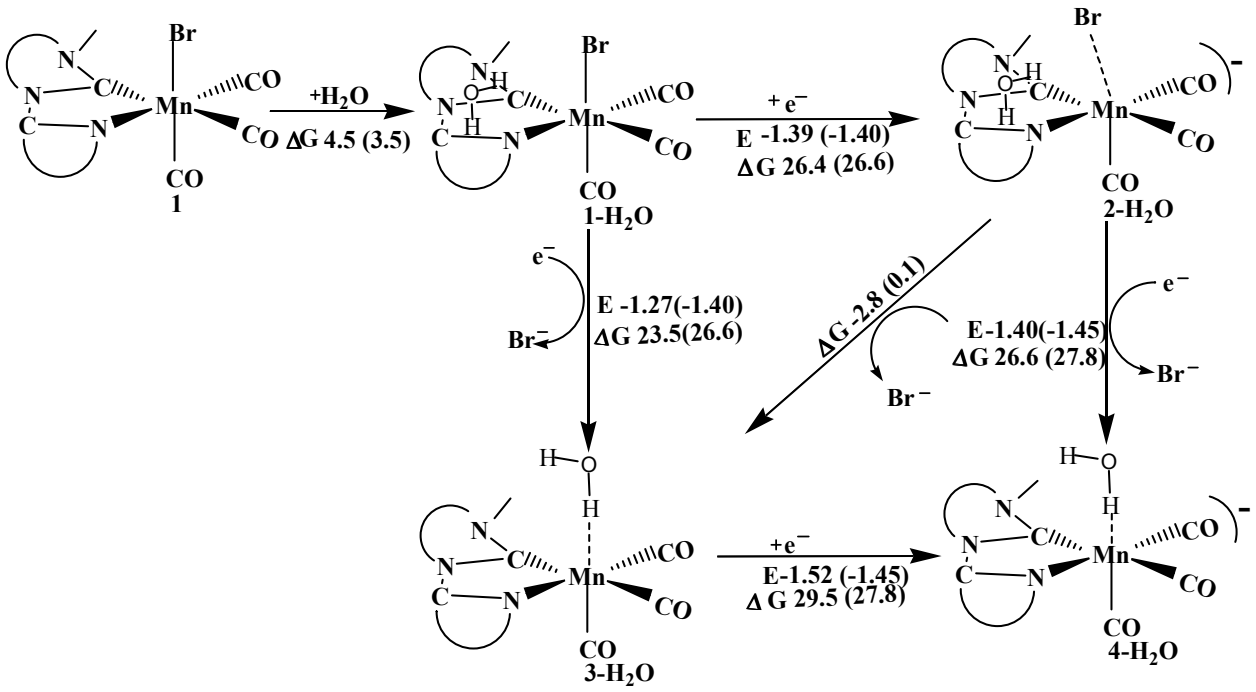


Figure S9. The calculated reaction free energies (ΔG in kcal/mol) and reduction potentials (E) are listed for possible products after one- and two-electron reductions of complex **1** (in the H_2O environment). Values in parentheses are calculated using GD3.

10. Table S4. Reaction free energies (ΔG in kcal/mol) and activation barriers ($\Delta G^{\ddagger}$ in kcal/mol) are listed for the protonation of complex **4** in different Brønsted acids. All bond distances (A-H, Mn-H) are in Angstroms (Å). Values in parentheses are calculated using GD3.

Proton Source	A-H Bond lengths			Mn-H	ΔG	($\Delta G^{\ddagger}$)
	Gas Phase	TS	Difference			
HCl	1.29	1.56	0.27	2.13	-36.3(-36.8)	0(0)
PhOH	0.97	1.47	0.50	1.78	-6.0(-6.1)	21.5(17.6)
TFE	0.97	1.62	0.65	1.72	0.9	23.7
H_2O	0.97	1.73	0.76	1.70	12.3(11.8)	29.5(27.1)
CH_3OH	0.97	1.75	0.78	1.69	12.7(12.4)	31.5(26.9)

11. Reaction Scheme

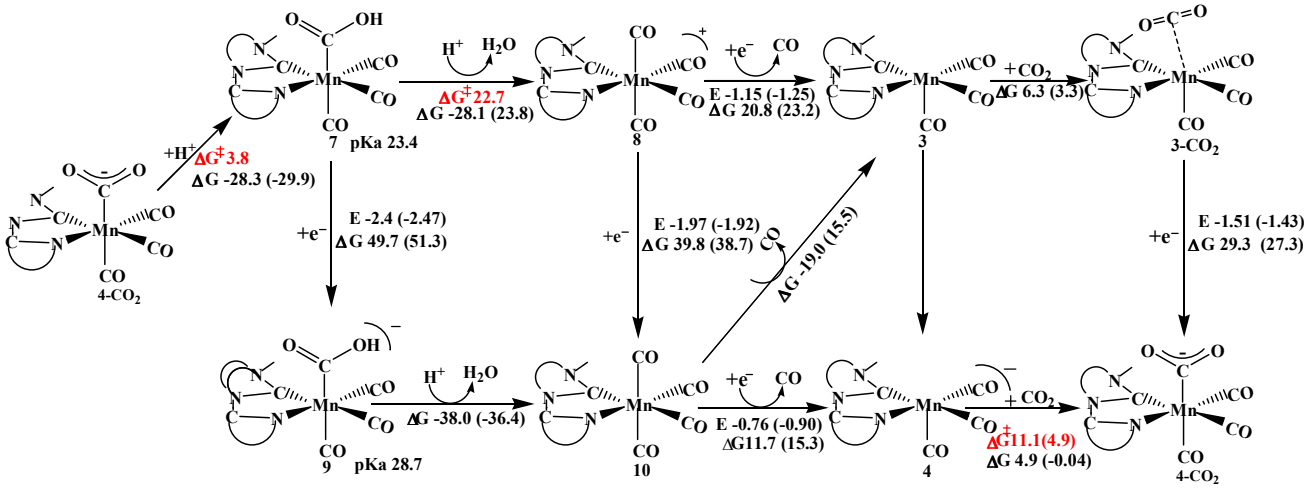


Figure S10. All possible reaction pathways are presented for CO_2 to CO reduction. Reaction energies (ΔG in kcal/mol), reduction potentials (E), activation barriers ($\Delta G^{\ddagger}$ in kcal/mol) and pK_a values are given for their respective steps. Values in parentheses are calculated using GD3.

12. References

1. Namazian, M.; Coote, M. L. Accurate Calculation of Absolute One-Electron Redox Potentials of Some para-Quinone Derivatives in Acetonitrile. *J. Phys. Chem. A,* **2007,** *111,* 7227−7232.
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3. Tawa, G. J.; Topol, I. A.; Burt, S. K.; Caldwell, R. A.; Rashin, A. A. Calculation of the aqueous solvation free energy of the proton. *J. Chem. Phys.* **1998,** *109,* 4852−4863.
4. Kelly, C. P.; Cramer C. J.; Truhlar, D. G. Single-Ion Solvation Free Energies and the Normal Hydrogen Electrode Potential in Methanol, Acetonitrile, and Dimethyl Sulfoxide. *J. Phys. Chem. B* **2006,** *111,* 408−422.
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6. Keith, J. A.; Grice, K. A.; Kubiak, C. P.; Carter, E. A. Elucidation of the Selectivity of Proton-Dependent Electrocatalytic CO_2 Reduction by fac-Re(bpy)$(CO)_3$Cl. *J. Am. Chem. Soc.* **2013,** *135,* 15823−15829.

13. Cartesian coordinates and energies (in Hartree) in solvent phase for all the species

G = -2571.612898 Br 0.00000 0.00000 0.00000

CH_3OH

G = -115.710897

C -0.04733 0.67063 0.00000
H -1.09293 0.98598 0.00000
H 0.44360 1.07538 0.89365
H 0.44360 1.07538 -0.89365
O -0.04733 -0.76136 0.00000
H 0.86830 -1.06965 0.00000

CH_3O^-

G= -115.212593

C -0.000015000 -0.567976000 0.000000000
H 1.021349000 -1.027670000 0.000000000
H -0.510571000 -1.027538000 0.884622000
H-0.510571000 -1.027538000 -0.884622000
O -0.000015000 0.811325000 0.000000000

HCl

G = -460.814906

H 0.000000 0.000000 -1.217408
Cl 0.000000 0.000000 0.071612

Cl^-

G = -460.394724

Cl 0.000000 0.000000 0.000000

PhOH

G = -307.425574

C 1.86095 0.02963 -0.00014
C 1.17627 -1.19175 -0.00008
C 1.13133 1.22248 0.00013
H 1.73024 -2.12613 -0.00015
H 1.64749 2.17823 0.00005
C -0.21969 -1.22575 0.00014
C -0.26703 1.20259 0.00009
H -0.75791 -2.16857 0.00019
H -0.82975 2.13273 0.00032
C -0.94015 -0.02510 0.00007
H 2.94622 0.05044 -0.00040
O -2.31036 -0.11376 0.00011
H -2.70344 0.77077 -0.00214

PhO^-

G = -306.957027

C -1.82785 -0.00003 -0.00013
C -1.10437 -1.20399 -0.00002
C -1.10486 1.20371 -0.00009
H -1.63988 -2.15252 0.00013
H -1.64019 2.15238 -0.00005
C 0.29044 -1.21151 0.00017
C 0.29041 1.21153 0.00026
H 0.83017 -2.15737 0.00035
H 0.82914 2.15787 0.00045
C 1.06394 0.00022 0.00006
H -2.91426 -0.00046 -0.00036
O 2.36110 0.00006 -0.00025

TFE

G = -452.777429

C 0.91578 0.74802 -0.00008
H 0.94173 1.38256 -0.89328
H 0.94172 1.38267 0.89306
C -0.41369 0.01742 -0.00001
F -1.43699 0.90896 -0.00087
F -0.57189 -0.77560 -1.08804
F -0.57260 -0.77417 1.08896
O 1.94252 -0.22694 -0.00003
H 2.79718 0.22505 0.00052

TEF-H

G = -452.298028

C 1.03401 0.68676 0.00490
H 0.98532 1.37136 -0.87748
H 0.98604 1.35975 0.89650
C -0.35013 0.02264 0.00047
F -1.37177 0.94080 0.00985

F -0.57062 -0.76130 -1.09624
F -0.56724 -0.78360 1.08238
O 2.06401 -0.19381 -0.00190

H_2O

G = -76.437730

O 0.000000 0.000000 0.117695
H 0.000000 0.766837 -0.470781
H 0.000000 -0.766837 -0.470781

OH^-

G = -75.940083

O 0.000000 0.000000 0.107496
H 0.000000 0.000000 -0.859968

CO_2

G = -188.599520

C 0.000000 0.000000 0.000000
O 0.000000 0.000000 1.169553
O 0.000000 0.000000 -1.169553

CO

G = -75.940083

C 0.000000 0.000000 -0.649854
O 0.000000 0.000000 0.487391

[MnBr(NHC-pyridine)$(CO)_3$] (1)

G = -3681.573795

Mn 1.42230 -0.44464 0.41665
Br 1.19042 -0.56133 -2.19468
N -1.53808 -1.53411 0.48054
N -1.25172 0.60876 0.20733
N 0.83875 1.57089 0.27663
C -0.58483 -0.58528 0.42598
C -2.80662 -0.99016 0.24126
C -4.05487 -1.60536 0.16265
H -4.17212 -2.67450 0.29820
C -5.15209 -0.78727 -0.11272
H -6.14136 -1.22748 -0.18419
C -4.99031 0.59349 -0.31001
H -5.85679 1.20661 -0.53595
C -3.73625 1.20643 -0.23087
H -3.65597 2.26865 -0.41060
C -2.63664 0.39291 0.05885
C -0.49058 1.78951 0.18881
C -1.03693 3.07360 0.12389
H -2.10304 3.22981 0.09252
C -0.17174 4.16426 0.12640
H -0.57525 5.17015 0.07797
C 1.20449 3.94745 0.20126
H 1.91283 4.76750 0.20731
C 1.66113 2.63763 0.28190
H 2.72020 2.42659 0.35708
C -1.32537 -2.95734 0.73411
H -0.40093 -3.08919 1.28888
H -1.28004 -3.51447 -0.20552
H -2.15020 -3.33516 1.34007
C 1.51491 -0.36905 2.20179
O 1.56157 -0.32569 3.35950
C 1.79657 -2.20807 0.37004
O 2.07995 -3.32985 0.31328
C 3.20364 -0.08356 0.17534
O 4.32980 0.11805 0.01326

[MnBr(NHC-pyridine)$(CO)_3$]-CO2 (1-CO_2)

G = -3870.166077

Mn -1.721577 -0.364474 -0.523669
Br -0.916423 -1.141388 1.850061
N 1.212718 -0.986783 -1.497296
N 0.848095 0.942972 -0.552433
N -1.266851 1.598808 0.078750
C 0.235532 -0.227397 -0.967949
C 2.459103 -0.357334 -1.384476
C 3.730199 -0.792138 -1.756499
H 3.888193 -1.759240 -2.220229
C 4.799497 0.065851 -1.493229
H 5.805527 -0.236343 -1.765711
C 4.591651 1.307732 -0.871738

H 5.440516 1.952039 -0.666652
C 3.315258 1.739337 -0.498982
H 3.204762 2.693347 -0.004274
C 2.239629 0.888952 -0.773007
C 0.029460 1.959890 -0.032319
C 0.484445 3.235700 0.309172
H 1.517866 3.515906 0.185467
C -0.434457 4.160250 0.797765
H -0.101988 5.157184 1.067398
C -1.774272 3.793160 0.925042
H -2.522661 4.482161 1.298452
C -2.143163 2.507404 0.548957
H -3.175035 2.187894 0.619913
C 1.044700 -2.305742 -2.103841
H 0.034499 -2.396476 -2.492905
H 1.235615 -3.094760 -1.371682
H 1.745268 -2.404393 -2.934020
C -2.213817 0.168840 -2.158870
O -2.519395 0.510498 -3.223854
C -1.947150 -2.110076 -0.914806
O -2.128802 -3.233646 -1.130298
C -3.427073 -0.318082 0.147259
O -4.502148 -0.315104 0.570726
C 2.710090 -1.359184 2.818499
O 2.619172 -0.319444 3.346254
O 2.816943 -2.400409 2.296528

[MnBr(NHC-pyridine)(CO)$_3$]$^-$ (2)

G = -3681.694537

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Br -0.603912 -0.164168 -4.023706
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N -1.112987 0.696090 0.139752
N 0.971448 1.659133 0.236148
C -0.445097 -0.447935 0.568828
C -2.671850 -0.877257 0.422765
C -3.923538 -1.490321 0.449525
H -4.039838 -2.527555 0.743239
C -5.024197 -0.714265 0.078219
H -6.015601 -1.155860 0.085124
C -4.863624 0.626666 -0.303304
H -5.733139 1.210735 -0.587455
C -3.604776 1.237344 -0.332032
H -3.529159 2.271645 -0.634965
C -2.499674 0.464694 0.035337
C -0.340841 1.848868 -0.051126
C -0.846859 3.077631 -0.484448
H -1.890266 3.200244 -0.726005
C 0.027429 4.152725 -0.609237
H -0.346321 5.114624 -0.944171
C 1.379117 3.974981 -0.300414
H 2.093786 4.785824 -0.380686
C 1.802109 2.719460 0.110714
H 2.841406 2.538575 0.353879
C -1.197198 -2.744839 1.220130
H -0.208731 -2.809430 1.667750
H -1.275054 -3.456909 0.393354
H -1.947890 -2.985790 1.976263
C 1.482475 -0.494517 2.568240
O 1.462414 -0.673087 3.725111
C 1.860356 -1.967518 0.328862
O 2.105677 -3.072503 0.026600
C 3.298598 0.054770 0.746827
O 4.452685 0.230077 0.735025

[MnBr(NHC-pyridine)(CO)$_3$]$^-$-CO$_2$ (2-CO$_2$)

G = -3870.283408

Mn -2.235648 -0.385037 0.243861
Br 0.977703 3.412408 1.246069
N 0.155390 -2.361477 0.647812
N 0.375732 -0.822593 -0.888148
N -1.357243 0.607881 -1.372287
C -0.492847 -1.314011 0.083171
C 1.420783 -2.539377 0.085300
C 2.414581 -3.472512 0.376082
H 2.279744 -4.220410 1.149595
C 3.596372 -3.400854 -0.365693
H 4.394704 -4.109047 -0.168056
C 3.764916 -2.423160 -1.358277
H 4.693107 -2.383834 -1.919403
C 2.765136 -1.486833 -1.646002
H 2.942331 -0.747071 -2.413267
C 1.579484 -1.556262 -0.909417
C -0.097054 0.221946 -1.693641
C 0.627586 0.806695 -2.735882
H 1.629032 0.485087 -2.972487

C 0.030499 1.823537 -3.474406
H 0.576903 2.291340 -4.286622
C -1.269433 2.227314 -3.157137
H -1.772135 3.014513 -3.706915
C -1.918257 1.596141 -2.105918
H -2.925912 1.878828 -1.828772
C -0.374227 -3.220503 1.701104
H -1.439901 -3.032506 1.802424
H 0.127941 -3.016692 2.651320
H -0.219967 -4.267244 1.427829
C -3.205363 -1.801937 -0.245524
O -3.841838 -2.742473 -0.530723
C -2.330730 -0.587505 2.016054
O -2.408726 -0.713255 3.178267
C -3.673308 0.716554 0.327579
O -4.618368 1.396507 0.410442
C 3.950355 1.154171 1.181271
O 4.389970 1.731612 0.263977
O 3.533667 0.561555 2.099512

[Mn(NHC-pyridine)(CO)$_3$] (3)

G = -1110.087912

Mn 1.643576 -0.542549 -0.071284
N -1.313957 -1.558632 -0.010877
N -1.000243 0.602883 -0.075934
N 1.123150 1.482862 -0.033397
C -0.336963 -0.621320 -0.059636
C -2.581499 -0.972654 -0.013926
C -3.846129 -1.558234 0.012851
H -3.970807 -2.635105 0.036962
C -4.948455 -0.699998 0.003604
H -5.950216 -1.117049 0.023091
C -4.776407 0.692281 -0.032501
H -5.647588 1.339501 -0.039915
C -3.504810 1.276241 -0.061495
H -3.421414 2.353008 -0.091630
C -2.398609 0.422288 -0.052159
C -0.205620 1.756781 -0.059641
C -0.706259 3.061664 -0.065032
H -1.766306 3.255759 -0.091843
C 0.194889 4.121661 -0.036318
H -0.173646 5.142077 -0.039577
C 1.566414 3.853600 -0.003380
H 2.302417 4.648824 0.020572
C 1.980089 2.529570 -0.004772
H 3.033235 2.279818 0.018309
C -1.107057 -3.001316 0.053634
H -0.053925 -3.195846 0.239083
H -1.408539 -3.472750 -0.886175
H -1.698546 -3.417999 0.872654
C 1.814844 -1.337748 1.518736
O 1.926190 -1.890395 2.544793
C 1.821924 -1.974208 -1.123543
O 1.950560 -2.912857 -1.812876
C 3.425583 -0.240526 -0.218325
O 4.579712 -0.091098 -0.305236

[Mn(NHC-pyridine)(CO)$_3$]-CO$_2$ (3-CO$_2$)

G = -1298.677359

Mn -1.672183 -0.604001 -0.295500
N 1.303489 -1.559068 -0.451708
N 0.943947 0.596137 -0.422574
N -1.198989 1.428882 -0.428518
C 0.307857 -0.642310 -0.388557
C 2.557147 -0.946044 -0.499259
C 3.833208 -1.504694 -0.550422
H 3.981021 -2.578869 -0.557476
C 4.916183 -0.622811 -0.586730
H 5.925998 -1.018519 -0.625964
C 4.714628 0.765926 -0.569066
H 5.571371 1.431688 -0.594451
C 3.431672 1.322813 -0.516494
H 3.325289 2.397839 -0.498348
C 2.344637 0.445136 -0.483372
C 0.123422 1.731455 -0.456705
C 0.594428 3.045653 -0.523576
H 1.650157 3.262814 -0.544199
C -0.330697 4.084308 -0.566363
H 0.014781 5.111429 -0.618919
C -1.696161 3.786228 -0.542574
H -2.450245 4.563993 -0.575416
C -2.079700 2.454884 -0.472923
H -3.127216 2.181989 -0.453020
C 1.126603 -3.006778 -0.486562
H 0.075975 -3.227054 -0.656499
H 1.449255 -3.455388 0.457423
H 1.716975 -3.425088 -1.305446
C -1.908399 -1.390334 -1.881746

O -2.061318 -1.937563 -2.905067
C -1.780944 -2.050024 0.746439
O -1.867326 -2.997929 1.429611
C -3.446417 -0.327909 -0.042311
O -4.595118 -0.194270 0.114481
C 0.375535 0.215888 3.648053
O 1.045319 -0.741392 3.593922
O -0.292297 1.174308 3.706105

[Mn(NHC-pyridine)(CO)$_3$]$^-$ (4)

G = -1110.201526

Mn 1.625404 -0.586244 -0.001677
N -1.327031 -1.540568 0.002241
N -0.975318 0.631570 -0.002553
N 1.163200 1.433927 -0.005103
C -0.310205 -0.607172 -0.001428
C -2.574634 -0.936846 -0.000323
C -3.852569 -1.497711 -0.001167
H -3.994612 -2.573173 -0.000626
C -4.945344 -0.622275 -0.003256
H -5.952909 -1.027100 -0.003883
C -4.754822 0.765956 -0.005034
H -5.615235 1.427921 -0.006912
C -3.468391 1.327792 -0.004899
H -3.364918 2.403805 -0.006990
C -2.374391 0.461304 -0.002608
C -0.168632 1.760409 -0.002571
C -0.636237 3.081898 0.000808
H -1.694558 3.293600 0.004200
C 0.280234 4.125144 0.000856
H -0.062043 5.154681 0.003722
C 1.651913 3.811473 -0.002476
H 2.410694 4.586817 -0.002622
C 2.035510 2.484035 -0.005033
H 3.085426 2.218112 -0.006936
C -1.136780 -2.980925 0.003309
H -0.068885 -3.184768 0.038681
H -1.560792 -3.426537 -0.903363
H -1.620565 -3.429786 0.877505
C 1.752413 -1.639068 1.388890
O 1.846035 -2.424700 2.276316
C 1.748423 -1.681894 -1.360493
O 1.839725 -2.490760 -2.226949
C 3.392217 -0.267660 -0.017763
O 4.557378 -0.080632 -0.028593

[Mn(NHC-pyridine)(CO)$_3$]$^-$-CO$_2$ (4-CO$_2$)

G = -1298.793192

Mn 1.503972 -0.507235 0.232750
N -1.436782 -1.563770 0.351318
N -1.137574 0.593264 0.141268
N 0.957914 1.513267 0.212243
C -0.456181 -0.621074 0.281382
C -2.703529 -0.998455 0.192454
C -3.963625 -1.593100 0.152510
H -4.087553 -2.666108 0.246879
C -5.067817 -0.753432 -0.026832
H -6.063896 -1.183138 -0.064771
C -4.902142 0.631435 -0.167715
H -5.771459 1.264374 -0.315557
C -3.634076 1.225806 -0.129518
H -3.551655 2.295521 -0.256979
C -2.528298 0.392423 0.057814
C -0.367833 1.757745 0.129196
C -0.889172 3.056953 0.077870
H -1.951542 3.234789 0.031883
C -0.004929 4.129813 0.101652
H -0.388145 5.144302 0.060542
C 1.368709 3.884642 0.187849
H 2.092279 4.691344 0.213802
C 1.797897 2.564956 0.246615
H 2.852135 2.326899 0.322645
C -1.224632 -2.992405 0.545046
H -0.313385 -3.144447 1.118005
H -1.145910 -3.513590 -0.413988
H -2.063132 -3.404517 1.109349
C 1.867542 -0.432726 1.984035
O 2.132381 -0.406862 3.122850
C 1.858968 -2.250811 0.164994
O 2.148901 -3.381188 0.128791
C 3.144237 -0.170305 -0.428930
O 4.201932 0.028881 -0.885520
C 1.018903 -0.581144 -1.962187
O 0.662181 0.501067 -2.490048
O 1.132595 -1.700125 -2.531295

[MnBr(NHC-pyridine)(CO)$_3$]-H$_2$O (1-H$_2$O)

G = -3758.004390

Mn	-1.51213	-0.44682	-0.49822
Br	-1.24682	-0.53049	2.11664
N	1.45472	-1.49595	-0.71832
N	1.15789	0.63942	-0.39557
N	-0.94779	1.57261	-0.37103
C	0.49511	-0.56241	-0.58236
C	2.72999	-0.93332	-0.57996
C	3.98941	-1.52951	-0.61521
H	4.11022	-2.59604	-0.76657
C	5.09425	-0.69580	-0.43490
H	6.09246	-1.12091	-0.45371
C	4.92979	0.68220	-0.22193
H	5.80365	1.30912	-0.07691
C	3.66453	1.27561	-0.18535
H	3.58760	2.33785	-0.00563
C	2.55474	0.44557	-0.37283
C	0.38050	1.80739	-0.30760
C	0.90827	3.09531	-0.19081
H	1.97143	3.26642	-0.15306
C	0.02794	4.17238	-0.13505
H	0.41828	5.18067	-0.04593
C	-1.34576	3.93917	-0.20061
H	-2.06569	4.74822	-0.16402
C	-1.78510	2.62648	-0.31976
H	-2.84253	2.40276	-0.37851
C	1.24391	-2.92025	-0.96970
H	0.29089	-3.06000	-1.47157
H	1.25981	-3.48327	-0.03280
H	2.03640	-3.28391	-1.62511
C	-1.64815	-0.38572	-2.28157
O	-1.72302	-0.35024	-3.43753
C	-1.86102	-2.21619	-0.42800
O	-2.12568	-3.34106	-0.35446
C	-3.29582	-0.10669	-0.23417
O	-4.42285	0.08166	-0.06501
O	1.92794	-0.50987	3.38454
H	1.03404	-0.49486	2.99233
H	2.34508	0.30964	3.08775

[MnBr(NHC-pyridine)(CO)$_3$]$^-$-H$_2$O (2-H$_2$O)

G = -3758.124943

Mn	-2.18193	-0.61190	0.16803
Br	2.29652	0.75073	2.77578
N	0.56937	-1.66680	-0.88309
N	0.21499	0.48673	-0.99234
N	-1.80732	1.37580	-0.35810
C	-0.35196	-0.71841	-0.58562
C	1.71527	-1.10279	-1.44486
C	2.89787	-1.70264	-1.87587
H	3.04837	-2.77406	-1.80422
C	3.88504	-0.86497	-2.40406
H	4.81894	-1.29414	-2.75290
C	3.68166	0.52155	-2.49065
H	4.46309	1.15251	-2.90167
C	2.49392	1.11894	-2.05437
H	2.38555	2.19091	-2.13266
C	1.50365	0.28623	-1.52582
C	-0.57809	1.63535	-0.87037
C	-0.17305	2.92011	-1.24272
H	0.81133	3.10505	-1.64141
C	-1.06962	3.97301	-1.08916
H	-0.77394	4.97763	-1.37281
C	-2.34235	3.71811	-0.57051
H	-3.07214	4.50805	-0.43627
C	-2.66283	2.41475	-0.21991
H	-3.63721	2.17589	0.18697
C	0.41012	-3.10239	-0.67813
H	-0.63233	-3.30915	-0.45099
H	1.04233	-3.44507	0.14604
H	0.68923	-3.63221	-1.59220
C	-2.93489	-1.55381	-1.14892
O	-3.42064	-2.20208	-1.99414
C	-1.92494	-1.93850	1.33680
O	-1.77296	-2.80743	2.10752
C	-3.76522	-0.25418	0.97594
O	-4.79271	-0.06779	1.49744
O	4.84160	-0.78340	1.19228
H	4.53581	-0.88116	0.27957

H	4.10185	-0.33904	1.65893

[Mn(NHC-pyridine)(CO)$_3$]-H$_2$O (3-H$_2$O)

G = -1186.516569

Mn	-1.61393	-0.51829	-0.13125
N	1.34674	-1.54836	-0.19786
N	1.03634	0.60998	-0.05530
N	-1.08223	1.50097	-0.09988
C	0.37017	-0.61202	-0.12115
C	2.61524	-0.96562	-0.15490
C	3.87967	-1.55227	-0.18289
H	4.00419	-2.62770	-0.24252
C	4.98276	-0.69734	-0.12419
H	5.98400	-1.11565	-0.14230
C	4.81232	0.69304	-0.03822
H	5.68419	1.33762	0.00870
C	3.54149	1.27796	-0.00729
H	3.45954	2.35275	0.06488
C	2.43416	0.42716	-0.06731
C	0.24675	1.76735	-0.05393
C	0.75257	3.06991	-0.01901
H	1.81299	3.25900	0.01999
C	-0.14374	4.13405	-0.03744
H	0.22922	5.15252	-0.01181
C	-1.51568	3.87290	-0.09066
H	-2.24823	4.67143	-0.10811
C	-1.93468	2.55076	-0.11855
H	-2.98842	2.30617	-0.15911
C	1.13923	-2.98702	-0.32514
H	0.11290	-3.16868	-0.63275
H	1.33473	-3.49006	0.62629
H	1.81376	-3.38223	-1.08791
C	-1.78985	-1.03093	-1.83552
O	-1.90380	-1.39582	-2.93983
C	-1.86480	-2.12204	0.61493
O	-2.06514	-3.17298	1.09213
C	-3.38414	-0.19809	0.11026
O	-4.52956	-0.03425	0.25566
H	-0.69988	-0.67678	2.62221
H	-0.96192	0.10485	3.91779
O	-0.39444	-0.58084	3.53995

[Mn(NHC-pyridine)(CO)$_3$]$^-$-H$_2$O (4-H$_2$O)

G = -1186.632146

Mn	-1.54544	-0.65245	-0.18851
N	1.42227	-1.55882	-0.07964
N	1.03473	0.60618	-0.11990
N	-1.11210	1.37269	-0.24513
C	0.38966	-0.64400	-0.11498
C	2.65879	-0.93296	-0.02887
C	3.94512	-1.46998	0.03948
H	4.10653	-2.54229	0.06676
C	5.02112	-0.57486	0.07708
H	6.03435	-0.96146	0.13122
C	4.80660	0.80955	0.04988
H	5.65412	1.48707	0.08371
C	3.51197	1.34757	-0.01699
H	3.38919	2.42142	-0.03089
C	2.43487	0.46099	-0.05659
C	0.21236	1.71965	-0.20465
C	0.65874	3.04809	-0.24801
H	1.71259	3.27870	-0.21783
C	-0.27390	4.07276	-0.33651
H	0.05212	5.10697	-0.37222
C	-1.63866	3.73651	-0.38332
H	-2.40823	4.49758	-0.45518
C	-2.00059	2.40328	-0.33859
H	-3.04442	2.11735	-0.37859
C	1.25680	-3.00234	-0.10558
H	0.22987	-3.22534	-0.38771
H	1.46614	-3.44230	0.87592
H	1.93639	-3.44098	-0.84267
C	-1.68859	-1.48225	-1.72213
O	-1.80172	-2.14558	-2.69988
C	-1.66446	-1.96481	0.96856
O	-1.75374	-2.87934	1.72102
C	-3.30060	-0.34183	0.02004
O	-4.45580	-0.15726	0.17164
H	-1.27587	0.16993	2.24177
H	-1.20191	1.53868	2.95385
O	-1.16430	0.58885	3.12776

[Mn(NHC-pyridine)(CO)$_3$H] (5)

G = -1110.679560

Mn 1.600445 -0.626003 -0.151956
N -1.372250 -1.575559 0.069630
N -1.009047 0.572569 -0.051795
N 1.122864 1.419149 -0.058088
C -0.373311 -0.665399 0.009089
C -2.628228 -0.962547 -0.007054
C -3.906754 -1.516504 -0.021092
H -4.061705 -2.588420 0.028663
C -4.986320 -0.634154 -0.115002
H -5.997461 -1.028077 -0.131202
C -4.778500 0.750769 -0.198194
H -5.631536 1.416801 -0.279752
C -3.492623 1.302911 -0.185399
H -3.379049 2.374123 -0.267904
C -2.410466 0.424420 -0.083566
C -0.195538 1.712376 -0.040905
C -0.673516 3.026314 0.008476
H -1.730006 3.238617 0.039551
C 0.247789 4.068148 0.040297
H -0.101612 5.094551 0.081244
C 1.613032 3.774803 0.028188
H 2.364897 4.554846 0.058047
C 2.000402 2.441693 -0.017179
H 3.048587 2.169707 -0.018870
C -1.204132 -3.019430 0.199197
H -0.248479 -3.224976 0.674077
H -1.244845 -3.506890 -0.779137
H -2.000606 -3.414589 0.832183
C 1.985534 -0.759644 1.611868
O 2.248623 -0.884174 2.739357
C 1.837191 -2.353323 -0.509061
O 2.022220 -3.465058 -0.809058
C 3.268902 -0.296999 -0.756927
O 4.322074 -0.098528 -1.209674
H 1.215605 -0.527249 -1.697636

[Mn(NHC-pyridine)(CO)$_3$(OCO)]$^-$ (6)

G = -1298.757782

Mn -1.408064 -0.421911 -0.276994
N 1.506731 -1.598370 -0.274622
N 1.279286 0.559166 -0.020257
N -0.772261 1.574143 -0.218685
C 0.567000 -0.621149 -0.220687
C 2.788319 -1.087221 -0.057895
C 4.021533 -1.733517 0.014301
H 4.106680 -2.807788 -0.105554
C 5.147851 -0.942797 0.259146
H 6.124854 -1.411191 0.324024
C 5.029189 0.444201 0.431194
H 5.915653 1.038131 0.629997
C 3.788519 1.089420 0.360239
H 3.743025 2.157637 0.515141
C 2.659946 0.304998 0.106623
C 0.557794 1.759310 -0.050721
C 1.132691 3.031351 0.048431
H 2.196189 3.159206 0.170204
C 0.303950 4.146146 -0.027135
H 0.730798 5.140899 0.047666
C -1.070540 3.964962 -0.207989
H -1.752651 4.804540 -0.276976
C -1.556966 2.667889 -0.300439
H -2.614333 2.483040 -0.444292
C 1.246275 -3.014498 -0.505494
H 0.312995 -3.120374 -1.052183
H 1.182443 -3.559971 0.441011
H 2.054548 -3.432933 -1.108206
C -1.511635 -0.525506 -2.038506
O -1.588920 -0.623732 -3.202280
C -1.829994 -2.146129 -0.031783
O -2.126257 -3.269815 0.083806
C -3.184847 0.000449 -0.103004
O -4.315025 0.283222 -0.144608
C -1.976645 -0.510222 2.757993
O -3.084551 -1.020275 2.476531
O -1.081440 -0.196165 1.883217

[Mn(NHC-pyridine)(CO)$_3$(CO$_2$H)] (7)

G = -1299.260019

Mn -1.497149 -0.486295 -0.199786
N 1.449316 -1.596730 -0.288294
N 1.183023 0.561080 -0.117518
N -0.902701 1.532551 -0.164255
C 0.501191 -0.638413 -0.245972
C 2.729621 -1.048292 -0.140217
C 3.979496 -1.663501 -0.089057
H 4.088807 -2.739106 -0.167326
C 5.092496 -0.837591 0.080246
H 6.082554 -1.279511 0.126449

C 4.945643 0.552991 0.201276
H 5.824250 1.174195 0.342437
C 3.690161 1.166469 0.151072
H 3.624792 2.238465 0.265520
C 2.573241 0.344457 -0.028572
C 0.428545 1.745025 -0.112097
C 0.981718 3.028583 -0.094220
H 2.048414 3.181212 -0.084157
C 0.122723 4.123367 -0.108874
H 0.532249 5.127946 -0.094277
C -1.256014 3.911973 -0.151237
H -1.960739 4.735095 -0.166061
C -1.719456 2.602636 -0.184419
H -2.780991 2.395087 -0.230679
C 1.207456 -3.030166 -0.438146
H 0.351091 -3.186980 -1.089083
H 1.027829 -3.496632 0.534085
H 2.080470 -3.488883 -0.902237
C -1.623924 -0.418408 -2.011627
O -1.711342 -0.384733 -3.166340
C -1.866118 -2.237026 -0.197017
O -2.149672 -3.365521 -0.204342
C -3.251100 -0.094380 0.073384
O -4.372496 0.139959 0.252725
C -1.221444 -0.424718 1.885658
O -0.510041 0.364140 2.492968
O -1.885782 -1.326067 2.716167
H -2.448196 -1.902076 2.179938

[Mn(NHC-pyridine)(CO)$_4$]$^+$ (8)

G = -1223.288722

Mn -1.559013 -0.556919 0.000654
N 1.446621 -1.589707 -0.004589
N 1.112715 0.566217 -0.000802
N -1.007970 1.476248 0.000964
C 0.476427 -0.662758 -0.002823
C 2.712168 -0.988239 -0.002442
C 3.978747 -1.569840 -0.002091
H 4.110262 -2.645735 -0.003848
C 5.071953 -0.703875 0.001134
H 6.077180 -1.112075 0.001625
C 4.887612 0.688644 0.004127
H 5.754116 1.341765 0.007002
C 3.615230 1.265721 0.003722
H 3.528962 2.341919 0.006754
C 2.515671 0.400984 0.000123
C 0.319509 1.728099 -0.000749
C 0.830741 3.026823 -0.003074
H 1.891435 3.212541 -0.005909
C -0.061902 4.094513 -0.002749
H 0.317543 5.110639 -0.004610
C -1.433592 3.842399 -0.000172
H -2.163299 4.643195 0.000300
C -1.860283 2.521718 0.001351
H -2.915991 2.285660 0.002837
C 1.293819 -3.043590 -0.007802
H 0.242105 -3.301730 -0.018641
H 1.758479 -3.460649 0.888583
H 1.775148 -3.457582 -0.896709
C -1.958064 -2.334457 0.000575
O -2.270667 -3.443396 0.000781
C -1.473802 -0.546235 1.874240
O -1.399918 -0.544621 3.016762
C -3.368421 -0.190622 0.004634
O -4.499460 0.013870 0.007107
C -1.480903 -0.543722 -1.873269
O -1.411162 -0.540560 -3.016047

[Mn(NHC-pyridine)(CO)$_3$(CO$_2$H)]$^-$ (9)

G = -1299.343335

Mn -1.510245 -0.465326 -0.202734
N 1.447227 -1.590311 -0.338364
N 1.191733 0.572293 -0.093727
N -0.906082 1.526166 0.135532
C 0.501003 -0.606945 -0.270186
C 2.725417 -1.060495 -0.182782
C 3.983836 -1.667044 -0.160087
H 4.104686 -2.735280 -0.302502
C 5.092537 -0.848104 0.065227
H 6.083814 -1.290253 0.089336
C 4.942401 0.533933 0.273705
H 5.818247 1.145671 0.466594
C 3.683422 1.142229 0.243923
H 3.593736 2.203907 0.429040
C 2.572071 0.331261 -0.006362
C 0.454977 1.771410 -0.019380
C 0.995999 3.037530 -0.163828
H 2.055133 3.160801 -0.348768

C 0.160971 4.171073 -0.092851
H 0.565735 5.170245 -0.206766
C -1.234544 3.937217 0.111661
H -1.937066 4.761743 0.194577
C -1.704765 2.647331 0.199057
H -2.765028 2.458548 0.333324
C 1.156764 -3.007698 -0.519845
H 0.656965 -3.177166 -1.475726
H 0.521425 -3.371136 0.290491
H 2.090484 -3.568084 -0.510437
C -1.603498 0.005963 -1.945701
O -1.657051 0.350055 -3.055234
C -1.885749 -2.164750 -0.584507
O -2.183068 -3.252169 -0.898537
C -3.242627 -0.107740 0.155646
O -4.360396 0.108692 0.400823
C -1.233316 -0.779096 1.863957
O -0.572300 -0.112440 2.650336
O -1.850602 -1.887569 2.475121
H -2.364189 -2.351895 1.799153

[Mn(NHC-pyridine)(CO)$_4$] (10)

G = -1223.387836

Mn 0.255657 -1.669151 0.000000
N -2.101398 0.481533 0.000000
N -0.027512 1.238614 0.000000
N 1.769816 -0.221706 0.000000
C -0.790165 0.082881 0.000000
C -2.188486 1.866197 0.000000
C -3.299312 2.717004 0.000000
H -4.311979 2.329557 0.000000
C -3.061961 4.091716 0.000000
H -3.904694 4.776153 0.000000
C -1.752836 4.601395 0.000000
H -1.593125 5.674866 0.000000
C -0.641618 3.751365 0.000000
H 0.349419 4.180890 0.000000
C -0.869655 2.372542 0.000000
C 1.362347 1.112763 0.000000
C 2.275308 2.167666 0.000000
H 1.930565 3.190720 0.000000
C 3.644088 1.906597 0.000000
H 4.358541 2.722087 0.000000
C 4.068701 0.544419 0.000000
H 5.120389 0.278224 0.000000
C 3.120942 -0.451123 0.000000
H 3.423044 -1.491987 0.000000
C -3.243446 -0.423782 0.000000
H -3.232984 -1.053657 0.892609
H -3.232984 -1.053657 -0.892609
H -4.161873 0.160689 0.000000
C -1.142972 -2.816586 0.000000
O -2.006903 -3.587166 0.000000
C 0.249417 -1.488962 -1.859545
O 0.247779 -1.292581 -2.992155
C 1.415071 -3.079977 0.000000
O 2.134861 -3.983872 0.000000
C 0.249417 -1.488962 1.859545
O 0.247779 -1.292581 2.992155

TS-HCl

G = -1571.020338

Mn -1.583192 -0.553634 -0.277221
N 1.375599 -1.513283 -0.305250
N 0.993758 0.667441 -0.178184
N -1.132446 1.451537 -0.085404
C 0.312944 -0.597824 -0.213827
C 2.602265 -0.890264 -0.311853
C 3.897849 -1.408361 -0.397595
H 4.072454 -2.477904 -0.443909
C 4.973925 -0.509834 -0.422846
H 5.987222 -0.897760 -0.486640
C 4.761553 0.869647 -0.369958
H 5.605965 1.552315 -0.396773
C 3.459034 1.394726 -0.280895
H 3.325272 2.467340 -0.250765
C 2.385124 0.509347 -0.242801
C 0.195324 1.773563 -0.059972
C 0.638401 3.102720 0.085705
H 1.692388 3.327064 0.146722
C -0.299411 4.117951 0.178434
H 0.026670 5.147368 0.297274
C -1.667395 3.795481 0.126228
H -2.436406 4.557624 0.193238
C -2.025001 2.463923 0.001790
H -3.066210 2.163747 -0.030108
C 1.173592 -2.945971 -0.267740
H 0.619662 -3.283340 -1.149289

H 0.613536 -3.221674 0.630741
H 2.142450 -3.447320 -0.242488
C -2.281067 -0.341742 -1.897739
O -2.717968 -0.204568 -2.977150
C -1.845886 -2.314594 -0.350425
O -2.081428 -3.460246 -0.411541
C -3.050979 -0.388965 0.758373
O -3.997442 -0.288946 1.437481
H -0.276771 -0.778413 1.395800
Cl 0.212251 -0.920987 2.873471

TS-PhOH

G = -1417.593189

Mn -0.06186 -1.51629 0.81131
N 0.55836 1.46292 1.44939
N 1.76520 0.48733 -0.09731
N 1.46683 -1.71752 -0.59607
C 0.73583 0.25152 0.83406
C 1.37627 2.44897 0.89879
C 1.48308 3.80936 1.18613
H 0.86981 4.27802 1.94771
C 2.40517 4.55809 0.44537
H 2.51082 5.62005 0.64457
C 3.18235 3.95776 -0.55402
H 3.88362 4.55834 -1.12482
C 3.07165 2.59034 -0.84293
H 3.67626 2.16844 -1.63311
C 2.16117 1.83739 -0.09882
C 2.19809 -0.60372 -0.84146
C 3.28351 -0.59595 -1.72957
H 3.87146 0.29474 -1.88649
C 3.61008 -1.77227 -2.39302
H 4.44767 -1.78836 -3.08281
C 2.85654 -2.92726 -2.14978
H 3.07966 -3.86708 -2.64194
C 1.80814 -2.85265 -1.24495
H 1.20833 -3.72438 -1.01212
C -0.37354 1.71785 2.53796
H -0.45478 0.82596 3.15622
H -1.36408 1.98830 2.15814
H 0.00817 2.53438 3.15318
C 0.76921 -2.48295 2.06614
O 1.24948 -3.14378 2.90993
C -1.46227 -1.13834 1.82514
O -2.41901 -0.93366 2.47537
C -1.05872 -2.72063 -0.04895
O -1.74206 -3.45745 -0.65663
C -5.34140 1.60369 -1.02485
C -4.26405 2.48772 -1.18878
C -5.08470 0.22485 -1.04706
H -4.43945 3.56197 -1.17457
H -5.90602 -0.47858 -0.92157
C -2.96428 2.00977 -1.36700
C -3.78979 -0.26478 -1.23277
H -2.13594 2.70425 -1.49150
H -3.60583 -1.33584 -1.25398
C -2.68068 0.61367 -1.40379
H -6.35135 1.97875 -0.88460
O -1.45081 0.16683 -1.58162
H -0.91529 -0.61089 -0.45870

TS-TFE

G = -1562.941204

Mn 1.12698 -1.56441 -0.08690
N -1.87774 -1.43764 -0.87211
N -1.21886 -0.19368 0.80461
N 0.94233 -0.25594 1.53486
C -0.77204 -1.15001 -0.12185
C -2.97134 -0.65439 -0.50092
C -4.26127 -0.58683 -1.02514
H -4.56557 -1.20342 -1.86356
C -5.15172 0.31878 -0.43729
H -6.16348 0.39729 -0.82281
C -4.75062 1.13109 0.63210
H -5.45344 1.83536 1.06606
C -3.45223 1.06286 1.15568
H -3.17588 1.71916 1.96883
C -2.56449 0.15193 0.57962
C -0.29634 0.24617 1.74909
C -0.59461 1.08451 2.83266
H -1.59795 1.44306 3.00194
C 0.42711 1.42689 3.70956
H 0.21852 2.07248 4.55647
C 1.71383 0.91999 3.49191
H 2.53919 1.15857 4.15300
C 1.91894 0.08367 2.40466
H 2.89426 -0.34546 2.20886
C -1.93596 -2.42721 -1.93874

H -1.22549 -3.22317 -1.72626
H -1.70129 -1.97895 -2.90946
H -2.93948 -2.85522 -1.97553
C 1.24439 -3.04669 0.91288
O 1.34467 -4.05444 1.50470
C 1.19714 -2.39714 -1.64471
O 1.30153 -2.90507 -2.69767
C 2.85881 -1.15100 -0.29784
O 3.98204 -0.86996 -0.48122
C 1.72864 1.95935 -1.87845
H 2.30357 2.23111 -2.79084
H 2.47874 1.60235 -1.13941
O 0.70679 1.07909 -2.09084
H 0.91474 -0.20686 -1.12411
C 1.26556 3.30638 -1.31942
F 2.31480 4.16420 -1.10539
F 0.40774 3.96951 -2.14933
F 0.61923 3.20050 -0.12358

TS-H_2O

G = -1186.592217

Mn -1.559715 -0.590805 -0.126650
N 1.389069 -1.552229 -0.298504
N 1.039574 0.600965 -0.120720
N -1.081027 1.445509 -0.088896
C 0.380576 -0.632991 -0.239776
C 2.642057 -0.954122 -0.155174
C 3.917624 -1.514661 -0.111625
H 4.069409 -2.585459 -0.189470
C 5.001039 -0.644043 0.050658
H 6.007769 -1.048194 0.090011
C 4.801547 0.737774 0.174349
H 5.655055 1.394282 0.311168
C 3.517760 1.298439 0.133287
H 3.404574 2.366791 0.251059
C 2.434927 0.434088 -0.040923
C 0.239984 1.740506 -0.097113
C 0.718502 3.057815 -0.115167
H 1.775735 3.268406 -0.154936
C -0.201131 4.099775 -0.108883
H 0.147448 5.127287 -0.124866
C -1.569190 3.805030 -0.094611
H -2.320362 4.586621 -0.093854
C -1.957406 2.472980 -0.092256
H -3.005266 2.197837 -0.098526
C 1.208996 -2.985850 -0.481782
H 0.311636 -3.160175 -1.071563
H 1.119119 -3.500381 0.480006
H 2.066709 -3.387692 -1.024156
C -2.119455 -0.583290 -1.832547
O -2.520440 -0.637754 -2.932691
C -1.804774 -2.325821 0.120117
O -2.010140 -3.459423 0.341091
C -3.071638 -0.294289 0.784029
O -4.015624 -0.116024 1.454357
H -1.015161 -0.649820 1.486891
H -1.337768 -0.802549 3.535811
O -0.473277 -0.632371 3.133497

TS-CH_3OH

G = -1225.862163

Mn -1.472443 -0.668346 -0.318363
N 1.502411 -1.576662 -0.269536
N 1.103890 0.574701 -0.236926
N -1.029970 1.374006 -0.397465
C 0.476481 -0.677700 -0.312674
C 2.735810 -0.944349 -0.105264
C 4.017543 -1.475370 0.029547
H 4.191172 -2.545727 0.021490
C 5.076170 -0.574448 0.188974
H 6.087204 -0.954211 0.298436
C 4.845780 0.807893 0.219447
H 5.679914 1.489165 0.354783
C 3.555699 1.338551 0.085574
H 3.419429 2.409626 0.130775
C 2.497298 0.443278 -0.083877
C 0.282949 1.696563 -0.334121
C 0.738196 3.021132 -0.394199
H 1.791144 3.253211 -0.365770
C -0.197287 4.041361 -0.516802
H 0.133379 5.073676 -0.567140
C -1.557203 3.717841 -0.585833
H -2.320096 4.481282 -0.687345
C -1.921026 2.380404 -0.527664
H -2.961013 2.083404 -0.589231
C 1.361447 -3.021338 -0.391067
H 0.468966 -3.242214 -0.972259
H 1.285140 -3.497042 0.591646
H 2.230307 -3.422460 -0.916632

C -1.876808 -0.831925 -2.058235
O -2.178571 -1.002324 -3.178406
C -1.687742 -2.374931 0.092223
O -1.869890 -3.484618 0.426664
C -3.090192 -0.350334 0.386095
O -4.127019 -0.172780 0.900519
C -1.438540 0.655167 3.518042
H -2.185872 0.363552 4.293999
H -0.816782 1.447102 3.998657
H -2.024791 1.179270 2.729167
O -0.702235 -0.408344 3.023101
H -1.091064 -0.580533 1.329970

TS-CO_2

G = -1298.783356

Mn -1.538864 -0.511224 -0.391108
N 1.413167 -1.543821 -0.459160
N 1.085861 0.622354 -0.220779
N -1.019596 1.483722 -0.249903
C 0.388953 -0.609291 -0.356778
C 2.664278 -0.962976 -0.323213
C 3.939417 -1.533072 -0.313366
H 4.080131 -2.603774 -0.412877
C 5.038254 -0.677238 -0.161473
H 6.040298 -1.095661 -0.149913
C 4.860120 0.703670 -0.016930
H 5.723238 1.350574 0.105805
C 3.577519 1.276196 -0.019913
H 3.481189 2.345703 0.102404
C 2.478336 0.430121 -0.174504
C 0.310570 1.764027 -0.167899
C 0.796174 3.078999 -0.061746
H 1.854768 3.278449 -0.004334
C -0.109546 4.129498 -0.037398
H 0.247984 5.151091 0.043105
C -1.483909 3.849960 -0.124999
H -2.227199 4.639407 -0.113925
C -1.882281 2.528542 -0.231761
H -2.930748 2.265131 -0.310029
C 1.209407 -2.965554 -0.670657
H 0.357340 -3.112730 -1.333748
H 1.021999 -3.492692 0.271504
H 2.096040 -3.391667 -1.143926
C -2.235410 -0.389638 -2.006401
O -2.743406 -0.348552 -3.072716
C -1.821696 -2.250848 -0.250790
O -2.070598 -3.396707 -0.127463
C -2.947953 -0.256349 0.675845
O -3.898654 -0.104454 1.361921
C -0.524985 -0.651625 2.559091
O -0.686441 -1.799893 2.801145
O -0.247524 0.490164 2.703348

TS-OCO

G = -1298.753881

Mn -1.53751 -0.40994 -0.29628
N 1.40576 -1.46298 -0.46304
N 1.10919 0.68113 -0.09552
N -0.99638 1.57610 -0.03212
C 0.42027 -0.52805 -0.28359
C 2.67236 -0.90603 -0.31774
C 3.93983 -1.49021 -0.35941
H 4.06914 -2.55285 -0.53180
C 5.04686 -0.65765 -0.16443
H 6.04464 -1.08482 -0.19109
C 4.88424 0.71401 0.07338
H 5.75606 1.34089 0.23209
C 3.61152 1.29973 0.12018
H 3.52718 2.35768 0.32374
C 2.50234 0.47562 -0.08355
C 0.34032 1.83476 0.00879
C 0.85494 3.13383 0.12357
H 1.91871 3.31233 0.13162
C -0.02860 4.20208 0.21259
H 0.35174 5.21444 0.30110
C -1.40810 3.94751 0.17719
H -2.13681 4.74771 0.24302
C -1.83587 2.63631 0.04890
H -2.89299 2.40409 0.00570
C 1.14992 -2.88475 -0.62505
H 0.38911 -3.03621 -1.39142
H 0.79905 -3.31125 0.32097
H 2.06556 -3.38494 -0.93964
C -1.75234 -0.36775 -2.03485

O -1.90765 -0.38237 -3.19978
C -1.86789 -2.16227 -0.16907
O -2.17808 -3.29466 -0.17141
C -3.26322 -0.10985 0.15599
O -4.38781 0.06510 0.43439
C -0.68870 -1.17044 2.81652
O -0.24820 -2.28634 2.58373
O -1.22215 -0.24166 2.20819

TS for 4 to 6 formation

G = -1298.753881

Mn -1.537507 -0.409939 -0.296280
N 1.405763 -1.462984 -0.463041
N 1.109191 0.681134 -0.095525
N -0.996377 1.576098 -0.032117
C 0.420272 -0.528047 -0.283590
C 2.672362 -0.906027 -0.317736
C 3.939831 -1.490211 -0.359407
H 4.069136 -2.552852 -0.531797
C 5.046858 -0.657651 -0.164428
H 6.044644 -1.084817 -0.191093
C 4.884241 0.714006 0.073384
H 5.756063 1.340889 0.232088
C 3.611517 1.299733 0.120179
H 3.527183 2.357681 0.323736
C 2.502342 0.475619 -0.083554
C 0.340320 1.834764 0.008794
C 0.854945 3.133829 0.123568
H 1.918708 3.312326 0.131615
C -0.028602 4.202078 0.212589
H 0.351735 5.214436 0.301103
C -1.408096 3.947514 0.177195
H -2.136807 4.747709 0.243023
C -1.835875 2.636313 0.048898
H -2.892990 2.404092 0.005696
C 1.149915 -2.884748 -0.625047
H 0.389109 -3.036209 -1.391425
H 0.799049 -3.311253 0.320970
H 2.065561 -3.384944 -0.939636
C -1.752338 -0.367747 -2.034848
O -1.907649 -0.382365 -3.199784
C -1.867890 -2.162272 -0.169073
O -2.178077 -3.294661 -0.171411
C -3.263220 -0.109847 0.155991
O -4.387806 0.065099 0.434393
C -0.688697 -1.170445 2.816518
O -0.248199 -2.286343 2.583729
O -1.222152 -0.241663 2.208186

TS for proton transfer to 4-CO_2

G = -1375.224804

Mn 1.438631 0.110264 0.462593
N -1.209845 -1.539939 0.723063
N -1.368622 0.543974 0.081756
N 0.469986 1.907467 -0.016146
C -0.456317 -0.432267 0.490687
C -2.553963 -1.319238 0.411477
C -3.648476 -2.181298 0.453062
H -3.545581 -3.214289 0.765888
C -4.888689 -1.667000 0.062072
H -5.762423 -2.310784 0.079894
C -5.014029 -0.336555 -0.362563
H -5.983847 0.039128 -0.673152
C -3.911913 0.526543 -0.404511
H -4.049294 1.538740 -0.756443
C -2.672640 0.020514 -0.003654
C -0.870563 1.828607 -0.152754
C -1.660799 2.943995 -0.456329
H -2.734119 2.870522 -0.528495
C -1.033815 4.171332 -0.643758
H -1.627517 5.048367 -0.880414
C 0.354573 4.259011 -0.513426
H 0.882896 5.195849 -0.648078
C 1.058377 3.105083 -0.191847
H 2.134233 3.128900 -0.066656
C -0.707957 -2.823563 1.198547
H -1.477579 -3.305044 1.804163
H 0.168671 -2.659451 1.819764
H -0.446885 -3.477247 0.360892
C 1.615121 0.643115 2.167168
O 1.760576 0.974255 3.277744
C 2.172098 -1.470845 0.829059
O 2.707873 -2.474290 1.087719
C 3.026425 0.671389 -0.177421
O 4.054479 1.006277 -0.618449
C 1.175479 -0.511361 -1.644837
O 0.648383 0.320063 -2.423318
O 1.566565 -1.673587 -1.985674

H 2.108425 -3.300200 -1.804768
O 2.387777 -4.246574 -1.856982
H 2.223926 -4.505503 -2.772298

TS for protonation of 7

G = -1375.661488

Mn -1.157145 0.061917 -0.702472
N 1.476132 -1.687015 -0.509980
N 1.595504 0.392453 0.138451
N -0.214413 1.815495 0.001708
C 0.749067 -0.563429 -0.395585
C 2.777960 -1.493533 -0.026909
C 3.845764 -2.384286 0.073192
H 3.759874 -3.416079 -0.247378
C 5.033746 -1.893904 0.615872
H 5.888810 -2.554854 0.712404
C 5.133843 -0.561057 1.046819
H 6.065794 -0.205984 1.474534
C 4.060594 0.327808 0.946504
H 4.179835 1.338683 1.306970
C 2.870703 -0.156813 0.394095
C 1.095270 1.696087 0.312299
C 1.861595 2.780629 0.743119
H 2.912096 2.676576 0.958725
C 1.244434 4.021568 0.873546
H 1.823750 4.876283 1.206052
C -0.110852 4.149532 0.570152
H -0.630341 5.096163 0.659177
C -0.797203 3.023962 0.134094
H -1.846614 3.084234 -0.122947
C 1.008517 -2.970484 -1.033930
H 0.225369 -2.799412 -1.766226
H 0.633828 -3.600932 -0.223603
H 1.839895 -3.471230 -1.530310
C -0.691628 0.517142 -2.431745
O -0.387970 0.795822 -3.505062
C -1.882447 -1.511874 -1.250462
O -2.371296 -2.487126 -1.624908
C -2.817575 0.845894 -0.860274
O -3.851971 1.333193 -0.992573
C -1.466977 -0.370451 1.154456
O -1.358154 -0.490381 2.288783
O -3.774979 -1.371144 1.218959
H -4.318426 -1.582067 0.447679
H -4.455491 -1.767837 2.453242
O -4.903940 -2.065805 3.362564
H -5.452707 -1.325225 3.648673